

## PATENT SPECIFICATION

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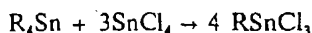


## (54) PROCESS FOR THE MANUFACTURE OF ALKYL-TIN TRIHALIDES

(71) We, SCHERING AKTIENGESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of Berlin and Bergkamen, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of alkyl-tin trihalides, especially trichlorides which are important precursors in the manufacture of polyvinyl chloride stabilisers.

The transfer of alkyl groups to the tin atom can be carried out in various ways (W. P. Neumann: Die organische Chemie des Zinns, Ferdinand Enke Verlag, Stuttgart, 1967, pages 16—35). However, a mixture of higher alkylated tin chlorides is generally obtained, especially in the production of alkyl-tin chlorides from tin tetrachloride and alkyl-aluminium compounds. In this case a mixture of trialkyl-tin chloride and tetra-alkyl tin is formed. The lower alkylation stages can then be obtained by so-called comproportionation (*loc. cit.*, pages 41—43). Alkyl-tin trichlorides are obtained, for example, by comproportionation of tetra-alkyl tin and tin tetrachloride:



However, the production of alkyl-tin trihalides by this process is limited to few aliphatic groups (for example, the vinyl group) and takes place only in a special solvent ( $POCl_3/P_2O_5$ ). The reason for this difficulty lies in the fact that the step necessary for complete comproportionation



can be accomplished only in exceptional cases.

Methods have been developed in which monoalkyl-tin trichlorides are formed in addition to dialkyl- or trialkyl-tin chlorides (German Patent Specification No. 1,161,893, British Patent Specification No. 739,883). Alkyl-tin trichlorides can be obtained from such mixtures, for example by distillation. However, owing to the high boiling points of long chain alkyltin trichlorides this method is very limited, and can be used industrially only for the production of short chain ( $\leq C_4$ ) alkyl-tin trichlorides.

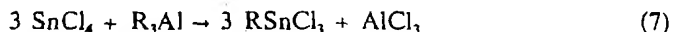
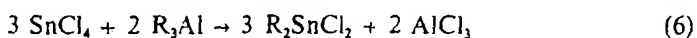
The simplest possibility for preparing alkyl-tin trichlorides would be the exchange of one chlorine atom in  $SnCl_4$  for an alkyl group: a monoalkylation. With the industrially easily accessible aluminium trialkyls, monoalkylation of  $SnCl_4$  has so far not been accomplished satisfactorily. However, alkyl-tin trichlorides can be prepared by monoalkylation of  $SnCl_4$  with alkyl-aluminium alkoxides (German Offenlegungsschrift 2,304,617; W. P. Neumann: Ann. Chem. 653 (1962) 163). However, this loses the great industrial advantage possessed by aluminium trialkyls in alkylation reactions as compared with other alkylating agents: with alkyl-aluminium alkoxides a maximum of only two alkyl groups per aluminium atom can be transferred.

According to German Auslegeschriften 1,157,617 and 1,164,407, it is possible to use alkyl-aluminium ether complexes and alkyl-aluminium amine complexes to prepare trialkyl-tin compounds and dialkyl-tin compounds or mixtures thereof,

depending on whether conversion is stoichiometric or non-stoichiometric. However, it has not hitherto been possible to prepare monoalkyl tin compounds by this method.

In a subsequent publication (Liebigs Ann. Chem. 653 (1962) 160) W.P. Neumann states:

"It has now been tested whether the reaction of aluminium alkyls with tin tetrachloride can be so controlled that in accordance with the equations



the various organo-tin halides can be prepared at will.

In the cases represented by equations (5) and (6) the expectation was in fact satisfied ....., when the  $\text{AlCl}_3$  formed was removed from the reaction mixture by complex formation with ethers or amines ....., It has not hitherto been possible to realise reaction 7."

We have found that the above-mentioned reaction (7) can be brought about by simultaneously maintaining a number of conditions during reaction.

The present invention provides a process for the preparation of an alkyl-tin trihalide, which comprises reacting an aluminium trialkyl or an alkyl-aluminium halide with a tin tetrahalide, the aluminium trialkyl or alkyl-aluminium halide being used in the form of a donor complex with an ether or a tertiary amine, and at no stage of the reaction being present in more than the stoichiometric amount required for monoalkylation of the tin tetrahalide.

Preferably the tin tetrahalide is tin tetrachloride.

More especially, the present invention provides a process for the preparation of an alkyl-tin trichloride by the monoalkylation of tin tetrachloride, wherein an aluminium trialkyl- or alkyl-aluminium halide-donor complex with an ether or a tertiary amine is reacted in the stoichiometric quantity required for monoalkylation, with tin tetrachloride.

Suitably the alkyl group or each alkyl group of the starting material contains up to 18 carbon atoms.

The reaction may, for example, be carried out discontinuously, the tin tetrahalide being placed in the reaction vessel initially, and the complex compound added thereto. By first providing the tin halide and subsequently adding the donor complex, the aluminium alkyl compound is never present in excess. Addition is continued up to an overall stoichiometric ratio of one mole of  $\text{SnCl}_4$  to no more than

$$\frac{1}{m}$$

moles of the aluminium alkyl compound wherein m represents the number of alkyl groups in the aluminium alkyl compound.

Reaction is generally conducted at a low temperature, preferably no more than  $100^\circ\text{C}$ . Suitably a temperature in the range of from  $20$  to  $100^\circ\text{C}$ , especially  $20$  to  $70^\circ\text{C}$ , more especially  $40$  to  $70^\circ\text{C}$ , is used.

Suitable donor complexes of the alkyl-aluminium compounds include, for example, complexes with diethyl ether, di-n-butyl ether, tetrahydrofuran, dioxan and anisole, and triethylamine, pyridine and dimethyl-aniline.

Some donor complexes, for example, those with tetrahydrofuran or pyridine, alkylate  $\text{SnCl}_4$  to form a mixture of products  $\text{R}_n\text{SnCl}_{4-n}$ , wherein n represents 1 to 4 and R represents an alkyl group, but in which the alkyl-tin trichloride is the main constituent.

Complexes of di-n-butyl ether with a trialkyl-aluminium compound or with an alkyl-aluminium halide have proved especially favourable: we have obtained the alkyl-tin trichloride in a yield of about 90 to 93% by weight. This may be increased to 97% when the  $\text{SnCl}_4$  is also used as an etherate complex. Complexes of  $\text{SnCl}_4$  with other ethers or with amines may also be used.

Suitably, the alkyl-aluminium compound is mixed with the desired donor in a manner known *per se* in a suitable apparatus under a protective gas. The alkyl-aluminium complex compound so formed is then reacted, also under a protective

gas, with the tin halide or, if desired, with a mixture of the tin halide and donor, e.g. di-*n*-butyl ether, in a molar ratio such that there is no more than one, preferably substantially one, alkyl group for each Sn atom. Advantageously, the SnCl<sub>4</sub> is first placed in the apparatus and the alkyl-aluminium complex compound is run in while mixing well. As this is an exothermic process cooling is generally necessary to maintain a low temperature during the reaction. Preferably the reaction is carried out at a temperature in the range of from 20 to 120°C, especially at substantially 40°C. At higher temperatures a larger proportion of by-products is formed and there is furthermore the risk of decomposing the donor complex.

When the conversion and after-reaction have terminated, the reaction mixture is advantageously diluted with a suitable solvent and introduced into ice-water. A suitable solvent is, for example, di-*n*-butyl ether. Dilution with di-*n*-butyl ether may be omitted if it has previously been added to the tin halide. The subsequent addition of di-*n*-butyl ether no longer influences the composition of the product. The ether addition is effected merely for better working up of the reaction product. If the addition of, for example, di-*n*-butyl ether is omitted, it is necessary, especially in preparing RSnCl<sub>3</sub> having a short chained R, to extract the aqueous phase several times with, for example, di-*n*-butyl ether. After the phase separation and distilling off of the di-*n*-butyl ether, there is obtained alkyl-tin trichloride in admixture with varying amounts of higher alkylated tin chlorides or tetra-alkyl tin.

The following Examples illustrate the invention.

#### Example 1.

171 g of (C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>Al.(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>O (corresponding to 0.33 mol of tri-*n*-octyl-aluminium) were added at 40°C, with stirring and cooling, to 260.5 g (1 mol) of SnCl<sub>4</sub> in a 1 litre three-necked flask having a stirrer, Claisen attachment, thermometer, reflux condenser and dropping funnel. When the introduction was finished, stirring was continued for about 30 minutes at 40°C, and then 260 g (2 mols) of di-*n*-butyl ether were added dropwise, also while stirring and cooling, at 40—50°C. When this addition was complete, the whole was stirred for a further 15 minutes without heating or cooling, and the reaction mixture was then introduced while cooling into 200 ml of ice-water. The temperature was kept at 50—70°C at most. After separation of the phases, the di-*n*-butyl ether was distilled off from the ether phase under reduced pressure, and C<sub>8</sub>H<sub>17</sub>SnCl<sub>3</sub> was obtained in the form of a pale to dark brown coloured liquid. The yield was 322 g (90% calculated on the Sn used).

Gas chromatographic analysis of a sample reacted with C<sub>2</sub>H<sub>5</sub>MgCl gave a content of C<sub>8</sub>H<sub>17</sub>SnCl<sub>3</sub> of 93% by weight.

#### Example 2.

In the apparatus described in Example 1 260 g (2 mols) of di-*n*-butyl ether was added, while stirring, to 260.5 g (1 mol) of SnCl<sub>4</sub> in the course of 5 minutes. The temperature rose to about 60°C. As this reaction mixture is solid between 40 and 50°C, further reaction with (C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>Al.(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>O was carried out at 50°C and in other respects as described in Example 1. The yield was 90%; the content of C<sub>8</sub>H<sub>17</sub>SnCl<sub>3</sub> determined by gas chromatography was 97%.

#### Example 3.

SnCl<sub>4</sub> was reacted with (C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>Al.(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>O as described in Example 1, but a further addition of di-*n*-butyl ether was omitted. After the hydrolysis of the reaction mixture, the aqueous phase was extracted 2—3 times with 70—100 ml of di-*n*-butyl ether each time, and the reaction product was isolated as described in Example 1. A yield of 90% was obtained; the content of C<sub>8</sub>H<sub>17</sub>SnCl<sub>3</sub> determined by gas chromatography was 97%.

#### Examples 4 to 18.

SnCl<sub>4</sub> was reacted as in Example 1 with a number of different aluminium-alkyl donor complexes at different temperatures. The complex and the temperature used are shown, together with the yield obtained, in Table I.

TABLE I

Example No.	Al-alkyl-compound	Donor	Temp. °C	% yield	RSnCl <sub>3</sub> in % by wt <sup>(3)</sup>
4	(C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> Al	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	40	90	95
5	(C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> Al	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	70	85	91
6	(C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> Al	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	30	80	87
7	(C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> Al	dioxan	40	80	84
8	(C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> Al	THF <sup>(1)</sup>	30	80	72
9	(C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> Al	anisole	30	80	91
10	C <sub>8</sub> H <sub>17</sub> AlCl <sub>2</sub>	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	40	90	99
11	(C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> Al	pyridine	30	60	77
12	(C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> Al	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	30	60	89
13	(C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> Al	DMA <sup>(2)</sup>	30	60	79
14	(C <sub>18</sub> H <sub>37</sub> ) <sub>3</sub> Al	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	50	80	85
15	(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> Al	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	40	85	87
16	(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> Al	THF <sup>(1)</sup>	30	80	68
17	(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> Al	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	30	70	65
18	(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> Al	anisole	40	80	73

<sup>(1)</sup> Tetrahydrofuran.

<sup>(2)</sup> Dimethyl-aniline.

<sup>(3)</sup> Surface % in the gas chromatogram.

The following Comparison Examples 1 to 3 illustrate the effect of deviating from the criteria which, according to the invention, are critical to obtaining a high yield of final product.

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## COMPARISON EXAMPLE 1.

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The process of Example 1 was carried out with the difference that the (C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>Al was not added as an etherate complex. The reaction product had the following composition:

RSnCl<sub>3</sub> = 10 weight percent

R<sub>2</sub>SnCl<sub>2</sub> = 5 weight percent

R<sub>3</sub>SnCl = 83 weight percent

R<sub>4</sub>Sn = 2 weight percent

Total yield calculated on the tin employed: 88 percent (RSnCl<sub>3</sub> + R<sub>2</sub>SnCl<sub>2</sub> + R<sub>3</sub>SnCl + R<sub>4</sub>Sn).

(R = C<sub>8</sub>H<sub>17</sub>—)

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## COMPARISON EXAMPLE 2.

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The process was carried out as in Example 1 with the difference that the SnCl<sub>4</sub>

was added to the alkyl aluminum donor complex. The reaction product had the following composition:

$\text{RSnCl}_3 = 73$  weight percent

$\text{R}_2\text{SnCl}_2 = 8$  weight percent

$\text{R}_3\text{SnCl} = 19$  weight percent

Total yield calculated on the tin employed: 95 percent ( $\text{RSnCl}_3 + \text{R}_2\text{SnCl}_2 + \text{R}_3\text{SnCl}$ ) +  $\text{R}_3\text{SnCl}$ .

( $\text{R} = \text{C}_4\text{H}_9$ )

### COMPARISON EXAMPLE 3.

Example 1 was repeated with the difference that the necessary stoichiometric ratio for the preparation of monoalkyl tin trichloride was not maintained. Products of the following composition were obtained:

Mol Ratio of $\text{SnCl}_4 : (\text{C}_6\text{H}_{17})_3\text{Al} \cdot (\text{C}_4\text{H}_9)_2\text{O}$	Temperature (°C)	Composition in Percent by Weight				Total Yield*
		$\text{RSnCl}_3$	$\text{R}_2\text{SnCl}_2$	$\text{R}_3\text{SnCl}$	$\text{R}_4\text{Sn}$	
1:0.66	40	28	55	14	3	98
1:1	40	7	60	12	21	98
1:1.33	40	2	37	13	48	99

\* Calculated on the tin employed, i.e. percent ( $\text{RSnCl}_3 + \text{R}_2\text{SnCl}_2 + \text{R}_3\text{SnCl} + \text{R}_4\text{Sn}$ )

The following Example illustrates the effect of varying the temperature.

Example 19.

Example 1 was carried out with the exception that the reaction temperature was raised to 100°C. A product of the following composition was obtained:

$\text{RSnCl}_3 = 75$  weight percent

$\text{R}_2\text{SnCl}_2 = 25$  weight percent

Total yield based on the tin employed: 90 percent ( $\text{RSnCl}_3 + \text{R}_2\text{SnCl}_2$ ).

WHAT WE CLAIM IS:—

1. A process for the preparation of an alkyl-tin trihalide, which comprises reacting an aluminium trialkyl or an alkyl-aluminium halide with a tin tetrahalide, the aluminium trialkyl or alkyl-aluminium halide being used in the form of a donor complex with an ether or a tertiary amine, and at no stage of the reaction being present in more than the stoichiometric amount required for monoalkylation of the tin tetrahalide.

2. A process as claimed in claim 1, wherein the reaction is carried out at a temperature in the range of from 20 to 70°C.

3. A process as claimed in claim 2, wherein the temperature is in the range of from 40 to 70°C.

4. A process as claimed in claim 3, wherein the temperature is substantially 40°C.

5. A process as claimed in any one of claims 1 to 4, wherein the ether is di-n-butyl ether.

6. A process as claimed in any one of claims 1 to 4, wherein the ether is diethyl ether, tetrahydrofuran, dioxan or anisole.

7. A process as claimed in any one of claims 1 to 4, wherein the tertiary amine is triethylamine, pyridine or dimethyl aniline.

8. A process as claimed in any one of claims 1 to 7, wherein the tin tetrahalide is in the form of a donor complex with an ether or amine.

9. A process as claimed in any one of claims 1 to 8, wherein the alkyl group contains 4, 8 or 18 carbon atoms.

10. A process as claimed in any one of claims 1 to 9, which is carried out under an inert gas atmosphere.

11. A process as claimed in any one of claims 1 to 10, wherein the process is discontinuous, the tin tetrahalide being placed in the reaction vessel initially and the alkyl-aluminium halide complex or aluminium trialkyl complex added thereto.

12. A process as claimed in any one of claims 1 to 11, wherein substantially the stoichiometric quantity of aluminium trialkyl or alkyl-aluminium halide required for monoalkylation is used.

13. A process as claimed in any one of claims 1 to 12, wherein the tin tetrahalide is tin tetrachloride.

14. A process for the preparation of an alkyl-tin trichloride by the monoalkylation of tin tetrachloride, which comprises reacting tin tetrachloride with an aluminium trialkyl or alkyl-aluminium halide in the form of its donor complex with an ether or tertiary amine, the reactants being used in the stoichiometric quantities required for formation of a monoalkyltin compound.

15. A process as claimed in claim 14, which is carried out at a temperature in the range of from 20 to 70°C.

16. A process as claimed in claim 15, wherein the temperature is in the range of from 40 to 70°C.

17. A process as claimed in claim 1, carried out substantially as described in any one of the Examples 1 to 19 herein.

18. An alkyl-tin trihalide whenever prepared by a process as claimed in any one of claims 1 to 17.

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